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Danielsen, Hilmar Kjartansson; Nunzio, Paolo Emilio di; Hald, John

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# Kinetics of Z-Phase Precipitation in 9 to 12 pct Cr Steels

HILMAR K. DANIELSEN, PAOLO EMILIO DI NUNZIO, and JOHN HALD

The Z-phase nitride is seen as a detrimental phase in 9 to 12 pct Cr steels as it is in competition with the beneficial MX particles. Two model steels, with 9 pct Cr and 12 pct Cr content, respectively, were designed to study the effect of Cr on Z-phase precipitation kinetics. The steels were isothermally aged at 873 K, 923 K, and 973 K (600 °C, 650 °C, and 700 °C) for up to 30,000 hours in order for Z-phase to replace MX. X-ray diffraction (XRD) analysis of extracted precipitates was used to quantitatively follow the evolution of the nitrides population. It was found that the 12 pct Cr steel precipitated Z-phase 20 to 50 times faster than the 9 pct Cr steel. Transmission electron microscopy (TEM) was applied to follow the Z-phase precipitation, using energy-dispersive X-ray spectroscopy (EDS) line scans and atomic resolution imaging.

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## I. BACKGROUND

THE 9 to 12 pct Cr martensitic steels are widely used for power plant applications as they provide a good combination of high-temperature creep properties, oxidation resistance, and low cost. The newest 9 pct Cr steel grades have allowed operation at supercritical steam conditions up to 873 K (600 °C) and 300 bar in state-of-the-art power plants. The efficiency of these plants yield savings of about 30 pct in specific CO<sub>2</sub> emissions compared to older subcritical plants (813 K [540 °C]/180 bar). Higher temperature and pressure conditions (923 K [650 °C]/325 bar) are sought to increase efficiency, and for this purpose improved 12 pct Cr steel grades have been extensively tested. However, the high Cr content has caused microstructural instabilities in the steels for relatively short exposure times (10 kh).

The 9 to 12 pct Cr martensitic steels rely on precipitate strengthening for long-term creep strength at high temperatures. The prime beneficial precipitates are finely dispersed small MX nitrides, (V,Nb)N, which are dimensionally stable at high temperatures. However, they are not thermodynamically stable and are slowly replaced by another nitride called Z-phase with a Cr(V,Nb)N composition. With time, the Z-phase will fully replace the MX particles, as they contain the same constituents, but this can be a very slow process, measured in years or even decades. As the Z-phase precipitation is very slow, they will appear as few coarse particles, which do not contribute significantly to creep strengthening as opposed to the MX nitrides, resulting in a net loss of creep strength.<sup>[1–3]</sup> Thus, the long-term creep strengths of these steels are dependent on the

Z-phase being slow to precipitate and not appearing in significant numbers within the lifetime of the power plants. It is now known that this precipitation process is significantly faster in 12 pct Cr steels, which have been favored for their high oxidation resistance needed in planned future power plants operating at higher temperatures. Thermodynamic modeling has shown the main driving force for Z-phase precipitation to be the Cr content dissolved in the matrix.<sup>[4]</sup> Investigations by electron microscopy have revealed the nucleation of Z-phase to be a diffusion of Cr atoms from the matrix into existing MX particles, physically transforming them into Z-phase.<sup>[5]</sup> The effects of Z-phase on the creep strength of 12 pct Cr steels has been well described because of the relatively fast precipitation, but recent investigations of commercial 9 pct Cr steel grades have indicated that the Z-phase might also affect these steels within their expected service life.<sup>[6]</sup> As these steels already are extensively used around the world, this could affect the lifetime of existing power plants. The objective of this article has been to quantify the effect of Cr on the Z-phase precipitation speed in these steels.

## II. EXPERIMENTAL

Two model alloys with 9 and 12 pct Cr, respectively, were designed with very similar compositions. As the alloys were meant for studying the nitride behavior using X-ray diffraction (XRD) measurements, the aim was to obtain an alloy devoid of other precipitate types. Without overlapping signals from other precipitates, the MX to Z-phase transformation could be followed. Thus, a very low C content was sought to avoid carbide formations, and elements like W and Mo were not added to prevent Laves phase from precipitating. A relatively high nickel content was needed to ensure a fully martensitic microstructure in the alloys.

The first alloy, 12CrVNbN, was designed for a fast precipitation of Z-phase using a thermodynamic model,<sup>[4]</sup> as the precipitation process could otherwise take decades.

HILMAR K. DANIELSEN, Senior Researcher, is with Mechanical Engineering, Technical University of Denmark (DTU), 2800 Kgs Lyngby, Denmark. Contact e-mail: hkd@mek.dtu.dk PAOLO EMILIO DI NUNZIO, Senior Researcher, is with Centro Sviluppo Materiali S.p.A. (CSM), 00128 Rome, Italy. JOHN HALD, Head, is with DONG Energy, 2820 Gentofte, Denmark.

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Thus, a 12 pct Cr alloy was used with additions of V, Nb, and N similar to commercial steel grades. This alloy could be used to study the transformation of Z-phase within a reasonable time period. The second alloy, 9CrVNbN, was similar to the first, except 9 pct Cr was used in this alloy, a similar content to what is found in most commercial steel grades. Thus, by comparing the two alloys, the effect of Cr on the Z-phase precipitation kinetics could be determined.

The model alloys were produced by vacuum induction melting as 80 kg ingots; the chemical compositions as determined by X-ray fluorescence spectroscopy are given in Table I. The ingots were hot rolled into 20-mm-thick plates and subsequently normalized at 1323 K (1050 °C) for 1 hour, followed by air cooling. Thereafter, they were tempered at 1023 K (750 °C) for 2 hours, followed by air cooling to obtain a tempered martensite microstructure. The microstructure consists entirely of tempered martensite, no delta ferrite was present, and the average hardness was around 235 HV<sub>10</sub>. After normalizing and tempering, the samples were aged at 873 K, 923 K, or 973 K (600 °C, 650 °C, or 700 °C) for up to 30,000 hours in laboratory furnaces flushed with air.

XRD spectra of the precipitated phases were recorded using a Bruker D8 Advance powder diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu radiation where Cu- $k\alpha_1$  and Cu- $k\alpha_2$  components had an intensity ratio of 2:1. To avoid interference from matrix reflections, the precipitates were extracted from the bulk by electrolysis in an acidic solution of 5 pct HCl in 95 pct ethanol, dissolving the matrix while gathering the precipitates by sedimentation. Some of the very small precipitates may not have been fully recovered by the sedimentation process. This could cause an underestimation of especially the VN amount, as they are usually very small.

A Rietveld refinement of the XRD spectra was used to quantify the volume fraction of each phase. By this technique, a set of parameters is refined to minimize the difference between the experimental data and a simulated diffractogram. The model crystal structures of the phases and their chemical compositions as measured by transmission electron microscopy (TEM)-energy-dispersive X-ray spectroscopy (EDS) are taken into account to calculate the absolute diffracted intensities. Then, the algorithm fits the measured spectrum in a given angular range by adjusting the peak shapes according to a theoretical function expressing the line profiles, taking also into account the absorption effects. Taking into account all the possible uncertainties in the different elaboration steps, the total error of the fitting procedure can be estimated to be maximally  $\pm 3$  units of volume percent. Details of the procedure can be found in Reference 7. In the calculations all precipitates were

considered to have constant chemical composition and the crystal structures reported in Reference 7. The absolute intensity of the main reflections of the  $\pi$ -phase found in 12CrVNbN alloy at 873 K (600 °C) were calculated from its typical chemical composition, as measured by EDS, and an estimated lattice parameter of about 0.628 nm.

In the analyzed spectra, the algorithm has been applied to the spectrum obtained by a Cu-K $\alpha$  doublet in the range of  $2\theta$  from 35 deg to 47 deg, where the majority of the main diffraction peaks of the phases are located.

The morphology and composition of the precipitates in the as-treated and aged samples were investigated with a field emission gun (FEG)-TEM (JEOL 3000F; JEOL Ltd., Tokyo, Japan). Furthermore, high-angle annular dark-field (HAADF) atomic resolution imaging was carried out using a FEI Titan 80-300ST TEM (FEI Company, Hillsboro, OR) with CEOS CESCOR probe spherical aberration corrector. All TEM observations were carried out on carbon extraction replicas. The replicas were prepared by a chemical etch with Vilella's reagent (1 pct picric acid and 5 pct hydrochloric acid in ethanol).

Identification of the precipitates in TEM investigations was done on the basis of EDS composition measurements of the metallic elements: Particles with  $[V] + [Nb] \geq 70$  at. pct were identified as MX. Two separate populations of MX nitrides were found, V-rich and Nb-rich, and particles with Nb rich cores and V rims were not uncommon. The MX-type precipitates VN and NbN have a NaCl-type crystal structure (face-centered cubic lattice of metal atoms with octahedral interstitial sites occupied by N), with lattice parameters of 0.413 and 0.439 nm, respectively. However, because the compositions of the MX precipitates found in the model alloys are rather (V,Nb)N and (Nb,V)N, the lattice parameters of both precipitate types are closer to each other.

M<sub>2</sub>X usually have a Cr<sub>2</sub>N composition with a hexagonal crystal structure and lattice parameters  $a = 0.481$  nm and  $c = 0.448$  nm. Cr<sub>2</sub>N nitrides could be identified by the following compositional criterion:  $[Cr] \geq 70$  at. pct of the metallic elements, the real composition being (Cr,V)<sub>2</sub>N. The V content does not affect the lattice parameter as Cr and V atoms are similar in size.

The modified Z-phase, Cr(V,Nb)N, was identified by the compositional relationship  $[Fe] + [Cr] \approx [V] + [Nb]$ , where  $45 < [Fe] + [Cr] \leq 65$  at. pct. Previous work has shown that the Z-phase does not nucleate in the matrix as most precipitates do, but rather it forms by Cr diffusion from the matrix into existing MX particles, which are then transformed compositionally and

**Table I. Composition of the Model Alloys in wt pct, Balance Fe**

	Cr	V	Nb	N	C	Ni	Mn	Si
12CrVNbN	11.85	0.183	0.076	0.061	0.0048	1.29	0.32	0.40
9CrVNbN	9.11	0.207	0.080	0.059	0.0040	1.27	0.34	0.41

crystallographically into Z-phase.<sup>[5,8,9]</sup> This results in Z-phase having two different crystal structures, which can coexist in a single precipitate particle.<sup>[10]</sup> The primary Z-phase crystal structure is tetragonal with lattice parameters of  $a = 0.286$  nm and  $c = 0.739$  nm, and it is likely the most thermodynamically stable. The secondary Z-phase crystal structure has a NaCl type lattice resembling that of the MX and is probably metastable. It has a slightly lower lattice parameter ( $a = 0.404$  nm) than the V-rich MX which it transforms from, as only half of the interstitial sites would be occupied by N.

### III. RESULTS AND DISCUSSION

After normalizing and tempering, both alloys contained only  $M_2X$  and MX nitrides, while the Z-phase precipitates during the annealing. TEM investigations were mainly carried out on 12CrVNbN exposed at 923 K (650 °C). The first fully developed Z-phases could already be detected by TEM after only 100 hours of exposure. A gradual Cr-enrichment was observed in some MX particles, which led to a composition in between MX and Z-phase (high Cr MX or low Cr Z-phase). These precipitates were found in both 12CrVNbN and 9CrVNbN and were believed to be MX particles in the process of transforming into Z-phase by diffusion of Cr from the matrix into the MX particles. Two different types of transformation processes could be observed: the first generally for smaller precipitates, which showed a core-rim structure with a Cr-poor MX composition at the core, and a Cr-rich Z-phase at the rim with a smooth concentration gradient of Cr from the MX to Z-phase area (see Figure 1(a)). These transforming precipitates are not necessarily symmetric and do not show any phase boundary between the core and rim. This Cr enrichment continues until the entire particle was transformed into Z-phase. More complicated forms of transformations

could be seen in larger MX precipitates, most of which contained Nb cores, where distinct areas of Z-phase will form at the edge of the MX particles. These Z-phase areas are typically be parallel (see Figure 1(b)), probably with a certain orientation relationship with the matrix. After the initial Cr in-diffusion, the parallel Z-phase areas will become well defined with sharp concentration gradients and could thus best be described as fully formed Z-phase attached to the MX. As this happens, the Z-phase starts to dissolve its MX host by matrix diffusion of V, Nb, and N. This gives the transforming particle an H shape, two parallel Z-phases connected by an MX bridge, until finally only two parallel Z-phases remain.<sup>[8]</sup> Figure 2 shows atomic resolution imaging of one of the H-shaped particles. The tetragonal double layered structure of Z-phase can clearly be seen as there is a contrast between Nb-containing MX layers and the Cr layers. The MX crystal structure appears monotonous as the V/Nb atoms and any dissolved Cr occupy the same lattice sites. The two crystal structures are directly joined, as the atomic layers continue through the “phase boundary” (see Figure 2(a)). A closer investigation of the Z-phase double-layered structure shows it is still not fully ordered into a tetragonal crystal structure as some of the MX layers (bright layers) are present as triple layers (see Figure 2(b)). Layers are also observed to change brightness from MX contrast to Cr contrast, indicating the crystal structure is still rearranging itself.

Figure 3 shows XRD powder diffraction of the thermally aged 12CrVNbN alloy at three different temperatures. For graphical representation, the spectra are normalized to the highest intensity peak {111} of  $M_2X$  (except for 873 K [600 °C]/30,000 hours), as  $M_2X$  was the most stable precipitate amongst the nitrides. The results from the thermal aging of the 9CrVNbN alloy are shown in Figure 4. As the Cr content is lower it contains fewer Cr nitrides and there is a peak overlap between  $Cr_2N$  and (Nb,V)N, as lattice parameters for MX are slightly lower compared to the 12CrVNbN

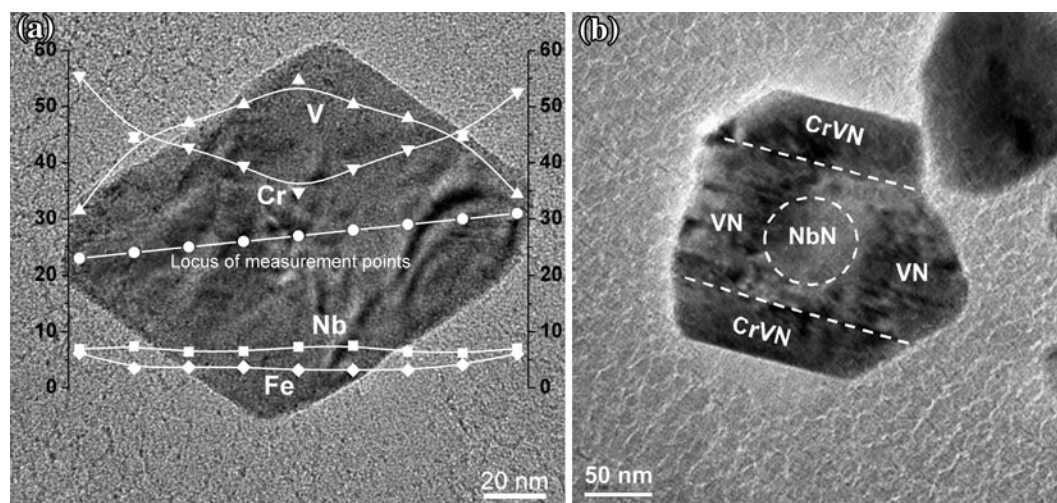


Fig. 1—Two typical transformation processes of small MX (a) and large MX (b) precipitates into Z-phase by in-diffusion of Cr in the 12CrVNbN alloy after exposure at 1000 h/923K (650 °C).<sup>[8]</sup> Scale in metallic at. pct.



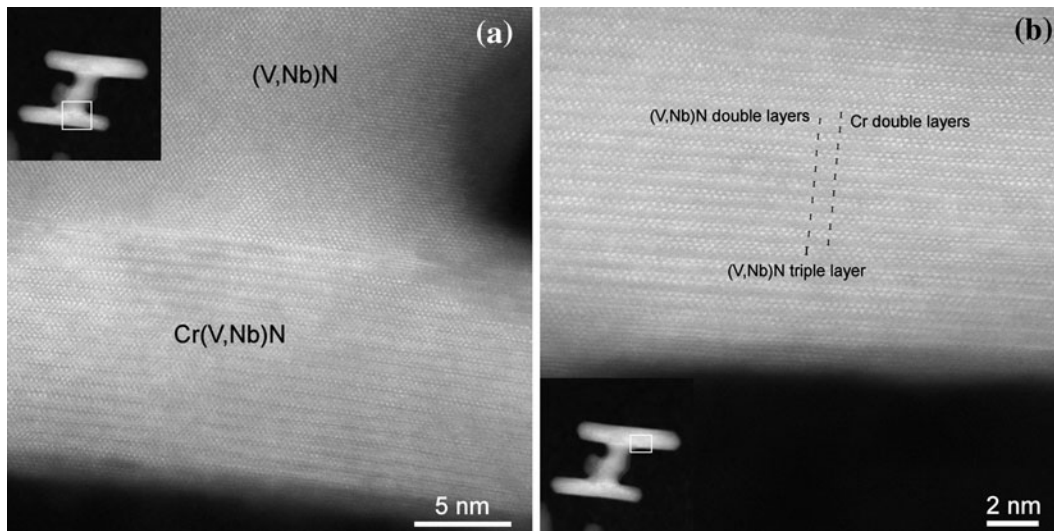


Fig. 2—HAADF atomic resolution imaging of an H-shaped hybrid Z-phase/MX particle found in 12CrVNbN after exposure at 1000 h/923 K (650 °C).

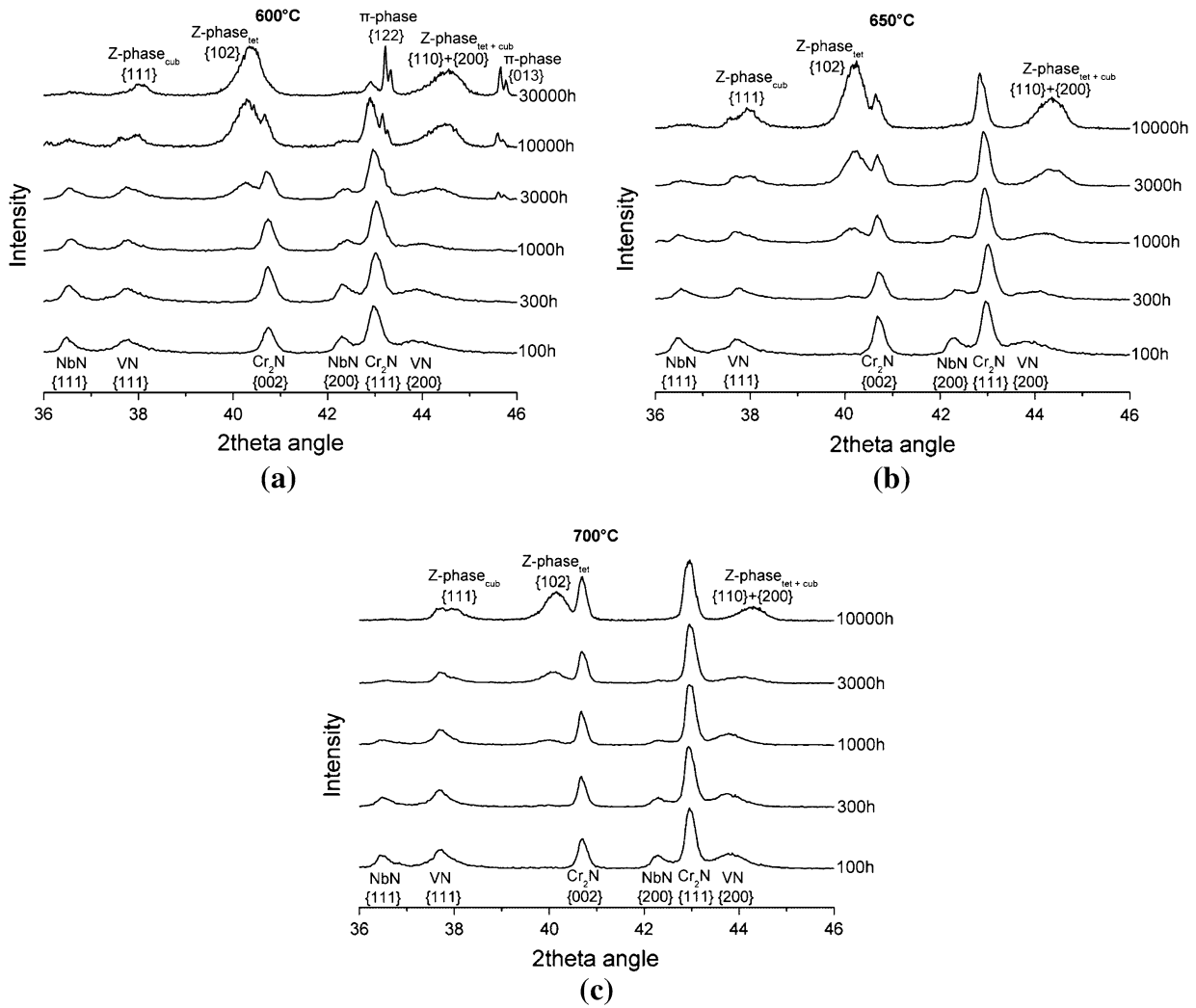


Fig. 3—XRD spectra of 12CrVNbN alloy isothermally aged at different times and temperatures.

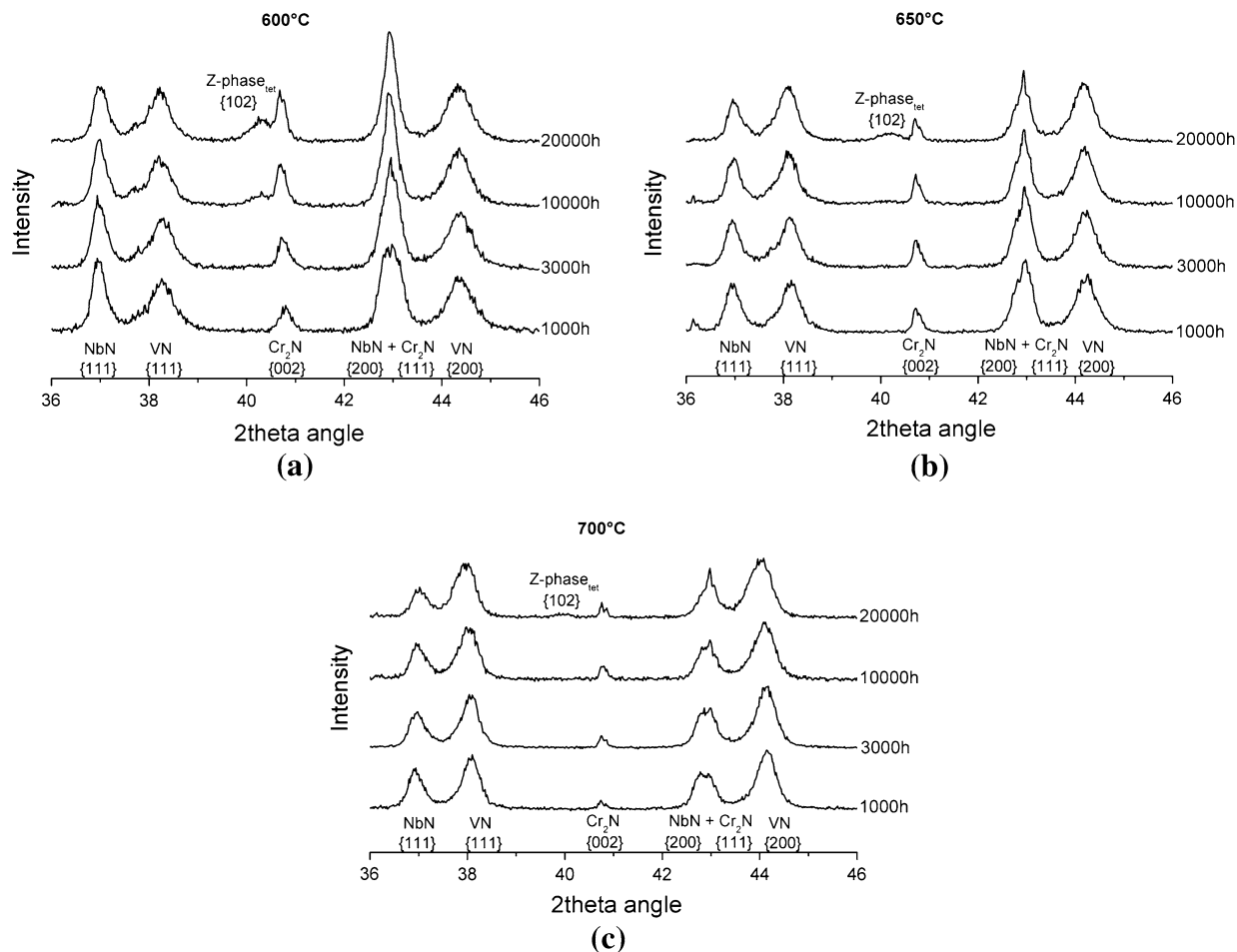


Fig. 4—XRD spectra of 9CrVNbN alloy isothermally aged at different times and temperatures.

**Table II. Rietveld Refinement of the 12CrVNbN Spectra in Fig. 3, Values Shown in Vol Pct of Precipitates**

	$\pi$ -phase	Cr <sub>2</sub> N	NbN	VN	Z-Phase Cub	Z-Phase Tet	Z/(MX + Z) (Pct)
<b>873 K (600 °C)</b>							
100 h	0.0	64.8	12.1	23.1	0.0	0.0	0
300 h	0.0	66.3	12.4	21.3	0.0	0.0	0
1000 h	1.2	66.6	12.1	14.0	0.0	6.2	19
3000 h	2.4	56.8	10.4	10.8	0.0	19.7	48
10,000 h	4.9	38.5	6.4	6.4	5.2	38.7	77
30,000 h	10.9	14.2	3.9	3.7	7.5	59.7	90
<b>923 K (650 °C)</b>							
100 h		64.7	13.1	22.2	0.0	0.0	0
300 h		77.3	9.6	10.5	0.0	2.6	7
1000 h		64.4	7.2	7.6	3.0	17.9	59
3000 h		54.2	4.6	3.5	4.5	33.2	82
10,000 h		37.0	2.6	0.0	13.9	46.5	96
<b>973 K (700 °C)</b>							
100 h		65.4	11.0	23.6	0.0	0.0	0
300 h		70.9	8.4	19.8	0.0	0.9	3
1000 h		75.0	5.0	12.2	0.0	7.8	31
3000 h		75.9	2.7	3.9	2.5	15.0	73
10,000 h		65.8	0.7	2.3	6.0	25.2	91

alloy. Thus, the {200} (V,Nb)N peak has been used as a reference point because it does not overlap with other peaks and was relatively stable. A Rietveld refinement of

the XRD spectra shown in Figures 3 and 4 was carried out to determine quantitatively the volume fractions of the extracted precipitates (see Tables II and III).

**Table III. Rietveld Refinement of the 9CrVNbN Spectra in Fig. 4, Values Shown in Vol Pct of Precipitates**

	Cr <sub>2</sub> N	NbN	VN	Z-Phase Cub	Z-Phase Tet	Z/(MX + Z) (Pct)
873 K (600 °C)						
1000 h	37.4	27.5	35.1	0.0	0.0	0
3000 h	38.7	27.0	31.5	0.0	2.7	4
10,000 h	39.5	24.1	27.9	0.0	8.5	14
20,000 h	37.6	22.2	27.1	0.0	13.1	21
923 K (650 °C)						
1000 h	35.6	25.9	38.4	0.0	0.0	0
3000 h	35.3	25.5	38.1	0.0	1.1	2
10,000 h	34.5	22.2	39.2	0.0	4.1	6
20,000 h	30.5	21.1	40.9	0.0	7.5	11
973 K (700 °C)						
1000 h	16.6	30.2	53.1	0.0	0.0	0
3000 h	19.5	27.0	53.4	0.0	0.0	0
10,000 h	18.5	24.4	54.8	0.0	2.3	3
20,000 h	18.4	20.3	57.0	0.0	4.3	5

The main feature in the 12CrVNbN alloy is that with time, Z-phase peaks replace the MX peaks and, to some extent, M<sub>2</sub>X. It can be seen that the main Z-phase peak (tetragonal peak at 40 deg 2 $\theta$  angle) is already visible after 300 hours at 923 K (650 °C), signifying a fast Z-phase precipitation in this alloy. The presence of the Z-phase cubic crystal structure can be verified at all temperatures. As the V-rich MX transforms into Z-phase, a gradual shift in VN peak positions toward a lower lattice parameter corresponding to the cubic Z-phase takes place as Cr enter the VN, yielding fewer interstitial sites that are occupied by N. As Z-phase precipitation was expected to be slower in the 9CrVNbN alloy, longer aging times were used compared to the high Cr alloy. Only one Z-phase peak was clearly visible: the main tetragonal peak {102} at about 40 deg 2 $\theta$  angle. Even after 20,000 hours, the nitride population consists mainly of MX as the peak positions of VN have only barely started to move to cubic Z-phase positions (873 K [600 °C] specimens). It has previously been speculated that the cubic crystal structure of Z-phase is a metastable precursor phase for the tetragonal crystal structure, which has difficulty in nucleating.<sup>[5]</sup> However, the data from the 12CrVNbN spectra show the amount of cubic Z-phase increases along with the amount of tetragonal Z-phase even in the range where Z-phase is well beyond the nucleation stage. For the 9CrVNbN alloy, the cubic Z-phase peak was too small to be quantified, as the Z-phase transformation has not progressed very far.

For the long-term exposed 12CrVNbN samples at 873 K (600 °C), a new precipitate appears with a A13  $\beta$ -Mn crystal structure. This is believed to be  $\pi$ -phase nitride, which has a  $\beta$ -Mn filled crystal structure.<sup>[11]</sup> A 30,000-hours sample was investigated to identify the new emerging phase. Very sharp XRD peaks could be observed, with the K $\alpha_1$  and K $\alpha_2$  peaks from the Cu radiation being individually distinguishable, indicating this phase being present as large particles. TEM investigations of the 873 K (600 °C)/30,000 hours sample show the presence of very large granular Cr-rich precipitates, average size of about 1  $\mu$ m (see Figure 5), with selected-area diffraction patterns corresponding to the emerging A13 peaks seen in the XRD spectra.

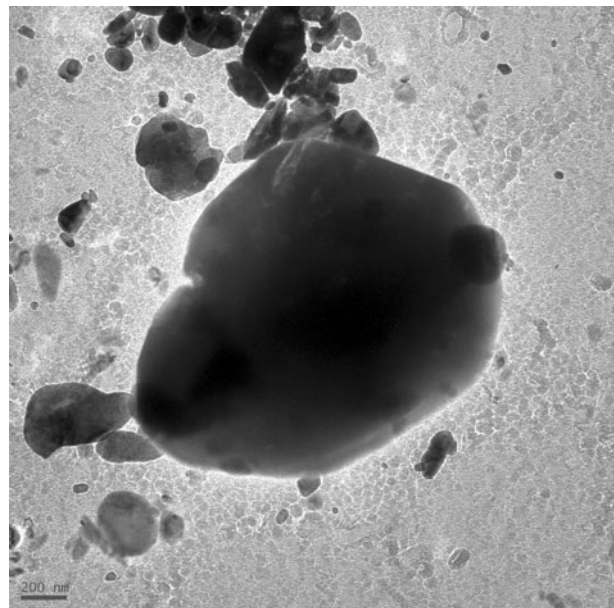


Fig. 5—A few very large particles believed to be  $\pi$ -phase were found among the other nitrides.

The precipitates had a chemical composition of 58 pct Cr, 17 pct Fe, 10 pct Si, 9 pct Ni, 6 pct V (at. pct of metallic component), and a small amount of N could be identified using electron energy loss spectroscopy. According to the literature,<sup>[12,13]</sup>  $\pi$ -phase is found in austenitic steels with a composition of roughly Cr<sub>3</sub>(Fe,Ni)<sub>2</sub>N, which corresponds well with the composition found in this work, considering 12CrVNbN only contains 1.3 pct Ni. Rietveld refinement was calculated based on the chemical composition and an estimated lattice parameter of about 0.628 nm. It shows an increase in quantity of  $\pi$ -phase with time, which probably will continue beyond 30,000 hours.

When comparing the VN/NbN ratio between the two steels, the 9 pct Cr steel seems to contain a larger amount of Nb-rich MX. The peak positions for Nb-rich MX

indicate a higher V content in 9 pct Cr steel, as they are closer to the VN peak positions, which could explain the increased amount. As the V-rich MX have a tendency to precipitate on the Nb-rich MX, forming particles with Nb-rich core and V-rich shell (see Figure 1(b)), the EDS composition measurements are difficult to compare.

The  $M_2X$  content is generally much higher for the 12 pct Cr steel even though the N content is the same for both alloys. Thermodynamic simulations using Thermo-Calc TCFE6 database (Thermo-Calc, Stockholm, Sweden) show that  $Cr_2N$  becomes more stable with higher Cr contents at the expense of the MX nitrides. At high Cr levels, the  $M_2X$  are stable to relatively high temperatures, while at low Cr levels, the dissolution temperature is close to the temperature range used in the current experiments. Thus, the  $M_2X$  level is very sensitive to temperature in the 9 pct Cr steels, but less so in the 12 pct Cr steel. Experimental data on 12CrVNbN show that  $M_2X$  amounts drop with time as the Z-phase becomes the dominant nitride, especially at lower temperatures. Calculations show at equilibrium conditions most N will be bound in the Z-phase, MX should be completely dissolved but a small  $M_2X$  amount remains. This  $M_2X$  amount is higher at 973 K (700 °C) compared to 873 K (600 °C), suggesting Z-phase is comparatively more stable than  $M_2X$  at a low temperature. These calculations do not take into account  $\pi$ -phase, and none of the thermally aged samples are believed to have reached equilibrium yet.

As the two model alloys are identical except for the Cr content, the results confirm the large effect of Cr on Z-phase precipitation speed seen in commercial steel grades.<sup>[3]</sup> Thermodynamic calculations also show Cr to be the most important element, and this is the main difference between Cr(V,Nb)N Z-phase and (V,Nb)N MX.<sup>[4]</sup> The results show that the Z-phase precipitation speed is fastest at 923 K (650 °C) for the 12CrVNbN alloy, which is consistent with time-temperature-precipitation (TTP) maps for Z-phase formation in 9 to 12 pct Cr commercial steels.<sup>[14]</sup> The Z-phase precipitation is much slower in the 9CrVNbN alloy at all temperatures, but it occurs fastest at 873 K (600 °C) compared to the other temperatures. The “nose” of the TTP diagram for 9 pct Cr

steels is thus at a somewhat lower temperature than for 12 pct Cr steels. This corresponds well to thermodynamic calculations, which show Z-phase in low Cr steels to have a lower solution temperature,<sup>[4]</sup> which would imply a displacement of the TPP diagram toward a lower temperature. However, this is not consistent with previous TTP maps for Z-phase formation in 9 pct Cr commercial steels based on presence/no presence measurements in TEM.<sup>[14]</sup> The current work shows there might be an underestimation of Z-phase quantity in commercial 9 pct Cr steel grades if accelerated tests at 923 K (650 °C) are used.

The target temperature for the development of most experimental 9 to 12 pct Cr steels is 923 K (650 °C) where the 12 pct Cr steel takes only little over 300 hours to reach the level of Z-phase precipitation that was obtained after 20,000 hours of exposure for the 9 pct Cr steel. At 873 K (600 °C), which is the highest temperature at which power plants can operate today, the level of Z-phase in the 20,000-hours 9 pct Cr sample corresponds to the 1000-hours 12 pct Cr sample. Thus, in the 873 K to 923 K (600 °C to 650 °C) temperature range, the Z-phase precipitation speed is 20 to 50 times faster in the 12 pct Cr alloy to reach 10 to 20 pct precipitation (depending on the temperature). The data from the Rietveld refinement in Tables II and III have been plotted in Figure 6, where TTP diagrams for Z-phase precipitation have been estimated for both alloys, respectively, based on the amount of MX transformed into Z-phase. The “nose” of the 9 pct Cr curve is hard to estimate without having data for 823 K (550 °C); thus, it could be lower than shown in Figure 6. Note that the data in Figure 6 cannot directly be correlated to commercial 9 and 12 pct Cr steels, as these steels contain about 0.1 wt pct C. Because carbon reacts with Cr to form carbides, the Cr content in the matrix is reduced by about 1 pct. Thus, the TTP diagrams in Figure 6 should represent 10 pct Cr and 13 pct Cr carbon-containing commercial grades. It must also be taken into account that newer experimental/commercial steels may also contain elements such as Co, which increases the precipitation speed of Z-phase,<sup>[15,16]</sup> and the current model alloys contains a relative large amount of nickel, which is considered to accelerate Z-phase precipitation speed.<sup>[17]</sup>

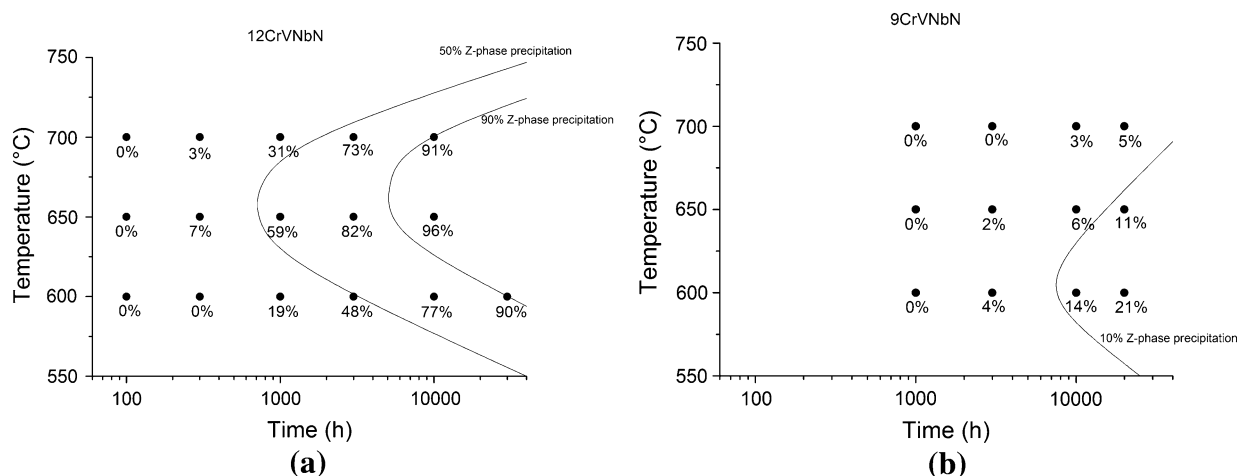


Fig. 6—TTP curves of the amount of MX transformed into Z-phase estimated from the Rietveld data.



#### IV. CONCLUSIONS

Z-phase precipitation speed was quantitatively investigated in a 12CrVNbN and a 9CrVNbN alloy, which were identical except for the Cr content. Z-phase precipitation speed in the 12 pct Cr alloy was found to be fastest at 923 K (650 °C), while for the 9 pct Cr alloy, it was fastest at 873 K (600 °C). Comparing the XRD spectra of the two model alloys quantitatively shows that the Z-phase precipitation speed is about 20 times faster at 873 K (600 °C) in the 12 pct Cr alloy compared to the 9 pct Cr alloy and about 50 times faster at 923 K (650 °C). During the transformation to Z-phase, the VN XRD peaks can be seen shifting from the (V,Nb)N positions toward the Cr(V,Nb)N positions, indicating a physical transformation of MX to Z-phase. Atomic resolution imaging showed the MX and Z-phase areas of particles were joined and that the crystal structure of the Z-phase was not fully ordered.

During long-term exposure at 873 K (600 °C) of the 12CrVNbN alloy, precipitation of what is believed to be the  $\pi$ -phase occurs. To the authors' knowledge, the  $\pi$ -phase has not been observed in this type of steel before.

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